



A reverse nonequilibrium molecular dynamics method for calculating the mutual diffusion coefficient for binary fluids



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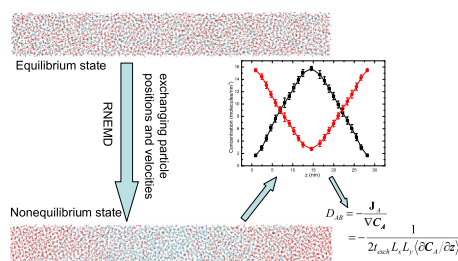
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HIGHLIGHTS

- A new nonequilibrium molecular dynamics method is developed.
- D_{AB} for nonequilibrium binary fluids is calculated directly.
- An artificial mass flux between different regions of the fluids is generated.
- D_{AB} is obtained through the mass flux and concentration gradient.

GRAPHICAL ABSTRACT



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ABSTRACT

This work introduces a nonequilibrium molecular dynamics method for calculating the mutual diffusion coefficient for mixtures. The method is based on the idea of the reverse nonequilibrium molecular dynamics algorithms, and artificially generates a mass flux through the Lennard–Jones mixtures by suitably exchanging particle positions and velocities in different regions. The analysis of the resulting steady-state concentration profiles allows the calculation of the mutual diffusion coefficient. As a test, this method is applied to the calculation of the mutual diffusion coefficient of Ar/Kr systems, and reasonable results are obtained. At the same time, it is observed that the mutual diffusion coefficient strongly depends on the temperature and composition of the mixture. The method can be easily extended to other fluid mixtures and be adopted when studying the nonequilibrium fluid mixtures.

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1. Introduction

Mass transfer in fluids and fluid mixtures is a very common phenomenon. With the development of biochemistry, alternative fuels, isotope separation and environmental pollution control, a

large number of accurate diffusion coefficients of various materials within wide range of pressure and temperature are getting more and more important and necessary. Therefore understanding the mass transport in mixtures by diffusion is important for many applications in chemistry, physics, biology, chemical engineering, etc. (Taylor and Krishna, 1993; Cussler, 2009). There are two self-diffusion coefficients and one mutual diffusion coefficient in binary mixtures. The former refers to the displacement of molecules of the two individual species, while the latter describes the transport of one species in a medium due to a concentration gradient. The self-diffusion coefficient can always be determined, even in equilibrium and in one-component fluids, whereas the

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mutual diffusion coefficient is much more meaningful in mixtures out of equilibrium.

For a binary system with nonuniform concentrations, there is a natural tendency for mass to be transferred to minimize the concentration differences within the system and to move it towards chemical equilibrium state (Benítez, 2009). Fick's law and the Maxwell–Stefan (MS) theory are often used to describe diffusive mass transport in a binary mixture (Taylor and Krishna, 1993). In both cases, a mass diffusive flux results from a gradient of a driving force. In the case of Fick's law, the driving force is the gradient of a mole fraction, while for MS theory the driving force is the gradient of the chemical potential in MS theory. The MS theory is capable of handling all processes of interest to chemical engineers and in many cases lead to superior predictions than the more conventionally used Fick's law (Krishna and Wesselingh, 1997). However, the MS diffusion coefficient cannot be obtained from experiments as the chemical potential gradients cannot be measured directly. Molecular dynamics (MD) simulation can be used straightforwardly to compute the MS diffusion coefficient from the motion of molecules inside the simulation box. In order to relate Fick to MS diffusion coefficient, the thermodynamic factor is needed and such a factor can be obtained from experiments and simulation. Note that the mutual diffusion coefficient is usually the Fick diffusion coefficient.

Diffusion coefficients can either be measured experimentally or estimated from theories or calculated by MD simulation. MD simulation is a good choice when experiments are impossible, unfeasible or simply too expensive (Cussler, 2009). Many equilibrium MD simulations have been performed to calculate self- and mutual diffusion coefficients for two or three component systems (for example: Jolly and Bearman, 1980; Schoen and Hoheisel, 1984; MacGowan, 1986; Hoheisel and Vogelsang, 1988; Pas and Zwolinski, 1991; van de Ven-lucassen et al., 1999; Min et al., 2007; Chae et al., 2011; Chae and Violi, 2011; Liu et al., 2011; Schnell et al., 2011; Pařez et al., 2013). Liu et al. (2013) reviewed the methods for predicting mutual diffusion coefficients from MD simulations, recently. Moggridge (2012a, 2012b) and D'Agostino et al. (2013) proposed an equation to predict the mutual diffusion coefficient in binary liquids from MS diffusion coefficients and the thermodynamic factor. Note that most of the simulation results agree well with the experiments suggesting that MD is an efficient tool to obtain mutual diffusion coefficient. In this paper, we propose a nonequilibrium method to calculate the mutual diffusion coefficient straightforwardly for binary fluids.

A variant of nonequilibrium molecular dynamics (NEMD), called reverse nonequilibrium molecular dynamics (RNEMD), has been developed earlier for transport processes, such as the thermal conductivity, the Soret coefficient and the shear viscosity (Müller-Plathe, 1997, 1999; Reith and Müller-Plathe, 2000; Zhang and Müller-Plathe, 2005; Terao et al., 2007; Zhang et al., 2013; Røsjorde et al., 2000, 2001; Bedeaux and Kjelstrup, 2004; Inzoli et al., 2011). Its advantages and shortcomings in comparison with alternative methods have been discussed (Müller-Plathe, 1997; Røsjorde et al., 2000). One NEMD method from Kjelstrup (Røsjorde et al., 2000, 2001; Bedeaux and Kjelstrup, 2004; Inzoli et al., 2011) should be mentioned, which is used to study on the two-phase systems. A “mass exchange” algorithm is adopted by removing a particle from one region and moving it to another region in the studied system. A mass flow from the vapor to the liquid was simulated. This method has been successfully used to study the evaporation of water recently. Similar to this method, in this contribution, the RNEMD method is extended from driving a heat (thermal conductivity) or momentum flux (shear viscosity) through the system, to artificially generating a mass flux through a mixture. This is done by exchanging particle positions and velocities in different regions, rather than particle velocity

components. This establishes a steady-state concentration profile, from which the mutual diffusion coefficient of the mixture is obtained. Details of our method are presented below. It is then validated by calculating the mutual diffusion coefficient of binary Lennard–Jones mixtures modelling Ar and Kr.

2. Methods

In a binary mixture, the diffusion is described by Fick's first law

$$-\mathbf{J}_A = D_{AB} \nabla C_A \quad (1)$$

in which D_{AB} is the mutual diffusion coefficient, ∇C_A is the concentration gradient of species A, \mathbf{J}_A is the diffusion flux vector of species A which is defined as the number of molecules transferred in a given time through a surface of a given area which is perpendicular to the flux direction. It is typically given in units of $\text{mol s}^{-1} \text{m}^{-2}$. In this paper, we are concerned with isotropic fluids and D_{AB} can be taken as scalar. The z direction is taken as the direction of the concentration gradient. Note, that it does not matter whether species A or species B is followed, since both fluxes are coupled and are described by the same mutual diffusion coefficient. In experiments and traditional NEMD, the concentration gradient ∇C_A would be imposed on the system, it would drive the mass flux \mathbf{J}_A , and the mutual diffusion coefficient D_{AB} can be obtained from the ratio of both species. In RNEMD, cause and effect are reversed, as described in the following.

The simulation box is divided into slabs equally along the z direction as shown in Fig. 1. The slab in the center of the box is defined as the “B slab”, where an excess of B is desired. In the “A slab”, an excess of A is desired. In the figure, the periodic system is shifted by half a slab width, so that one half of the “A slab”, labelled “A1 slab” and “A2 slab”, appears symmetrically at either end of the plots. The mass flux is generated by exchanging the position vectors and velocity vectors of a B atom in the “A slab” with those of an A atom in the “B slab” at periods of several thousand time steps, such that A enriches in the “A slab” and B in the “B slab”.

The above mechanism is a Maxwell daemon, which produces an artificial mass transfer between “A slab” and “B slab”. This leads to a concentration gradient in the intervening region. Exchanging position and velocity vectors leave the total momentum and the instantaneous kinetic energy of the system unchanged. However, after the exchange an atom A ends up in a surrounding adapted to the presence of atom B and vice versa, the potential energy and thus the total energy is changed in the process. This is particularly severe, when the inserted atom or molecule is larger than the removed one. This method, thus, must face on controlling and limiting the total energy increase due to particle exchanges, which will be discussed in the future.

The system reaches a steady state after sufficient time. The artificial mass transfer imposed by the position and velocity exchanges is exactly balanced by the mass flux in the opposite direction affected by the diffusion of the species. The imposed mass flux is known exactly, since one only has to sum the number of atoms transported by the exchanges. For a small enough exchange rate, a stationary linear concentration profile is obtained in the intervening slabs. The concentration gradient depends on

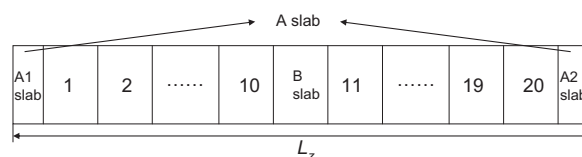


Fig. 1. The periodic simulation box subdivided into slabs.

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